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Journal of Chromatography A, 857 (1999) 175–181

JOURNAL OF CHROMATOGRAPHY A

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Ultra-short columns for low-pressure ion chromatography☆

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Received 18 November 1998; received in revised form 9 June 1999; accepted 17 June 1999

Abstract

Since the development of low-pressure ion chromatography (LPIC), many inorganic cations and anions as well as organic acids could be analyzed at a low-pressure of $1.96 \cdot 10^5$~$2.94 \cdot 10^5$ Pa. And the ultra-short columns took the place of the common long chromatographic columns. Furthermore, the ultra-short columns of LPIC not only reduced the system pressure appreciably, but also achieved high sensitivity and precision. In order to assess the characteristics of the super-short columns, much analysis, i.e., the analysis of alkali metals, alkaline earth metals, transition-metals, rare-earth elements, inorganic anions and organic acids as well as the common amino acids, were conducted. Moreover, excellent results were obtained from the LPIC columns.

Keywords: Columns; Metal cations; Organic acids; Inorganic anions; Amino acids

1. Introduction

Ion chromatography put forward by Small et al. [1] in 1975 has developed rapidly in recent years. It has been widely applied in such fields as environmental monitoring, food, chemical engineering, geology and medicine.

The research on ion chromatography [2] has also been done by Zhang and co-workers in recent years, and low-pressure ion chromatography (LPIC) [3–6], which works at a low-pressure of $1.96 \cdot 10^5$~$2.94 \cdot 10^5$ Pa, has been developed successfully. Moreover, many inorganic cations, i.e., alkali metals, alkaline earth metals, transition-metals, and inorganic anion as well as organic acids have been well separated and analyzed. In these cases, the low-pressure separation column (ultra-short column) play a very important part in the chromatographic analysis. In this paper, some research on the ultra-short columns was introduced.

2. Experimental

2.1. Apparatus

A Model ZJ-3 low-pressure ion chromatograph [4], devised by our laboratory, equipped with a model LDB-09 electronic pump (Xiangshan Instrument and Metert Plant, Zhejian, China) and a high sensitivity conductivity detector made by our laboratory, was used. A computer with a LPIC interface module was coupled with the chromatographic system for control of operating conditions. Data acquisition and measurement of chromatographic parameters were carried out by using the LPIC system

☆Presented at the International Ion Chromatography Symposium 1998, Osaka, Japan, 28 September – 1 October 1998.

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0021-9673/99/$ – see front matter
PII: S0021-9673(99)00747-5

Table 1
Chromatographic conditions for the analysis of alkali metals

Column	Measurement range	Column temperature	Eluent	Flow rate of eluent	Injection volume
LPIC separation column C_1 made by our laboratory (column dimensions: 3.0×0.5 cm I.D.; particle size: 20–30 μm; exchange capacity: 0.01 mmol g^{-1})	6.7·10 μs	Ambient	$1.44 \cdot 10^{-3}$ mol l^{-1} Na_2CO_3 aqueous solution	1.0 ml min^{-1}	20 μl

Table 2
Chromatographic conditions for the analysis of alkali earth metals

Column	Measurement range	Column temperature	Eluent	Flow rate of eluent	Injection volume
LPIC separation column C_2 made by our laboratory (column dimensions: 3.0×0.5 cm I.D.; particle size: 20–30 μm; exchange capacity: 0.01 mmol g^{-1})	2.5·10 μs	Ambient	A mixed aqueous solution of 0.8×10^{-3} mol l^{-1} ethylene diamine and 1.0×10^{-3} mol l^{-1} citric acid	1.0 ml min^{-1}	20 μl

software controller titled Data Working Station which was made by our lab.

3.1. Reagents and solution

All chemicals used were of analytical-reagent grade. All solutions used were made with deionized water provided by the Water Purification Agency of Sichuan University.

Working solutions were prepared weekly and stored at ambient temperature (10–35°C). The eluent was prepared by dilution of a working solution in deionized water. Moreover, only the eluent of Na_2CO_3 aqueous solution needs degassing.

4. Main chromatographic conditions

The main chromatographic conditions are given in Tables 1–9.

Table 3
Chromatographic conditions for the analysis of transition metals

Column	Measurement range	Column temperature	Eluent	Flow rate of eluent	Injection volume
LPIC separation column C_3 made by our laboratory (column dimensions: 4.0×0.5 cm I.D.; particle size: 20–25 μm; exchange capacity: 0.02 mmol g^{-1})	2·10 μs	Ambient	For the analysis of Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+} and Fe^{2+}, a mixed solution of 0.02 mol l^{-1} oxalic acid and 0.02 mol l^{-1} citric acid; for the analysis of Zn^{2+}, Pb^{2+}, Fe^{2+}, Cd^{2+} and Mn^{2+}, a mixed solution of 0.02 mol l^{-1} tartaric acid and 0.02 mol l^{-1} citric acid	1.0 ml min^{-1}	20 μl

Table 4
Chromatographic conditions for the analysis of inorganic anions

Column	Measurement range	Column temperature	Eluent	Flow rate of eluent	Injection volume
LPIC separation column made by our laboratory (column dimensions: 6.0×0.6 cm I.D.; particle size: 20–25 μm; exchange capacity: 0.02 mmol g^{-1}); LPIC separation column made by our laboratory (column dimensions: 5.0×0.6 cm I.D.; particle size: 20–25 μm; exchange capacity: 0.02 mmol g^{-1})	2×1 μs	Ambient	$1.4 \cdot 10^{-3}$ mol l^{-1} Na_2CO_3 aqueous solution	1.0 ml min^{-1}	20 μl

Table 5
Chromatographic conditions for the analysis of organic acids

Column	Measurement range	Column temperature	Eluent	Flow rate of eluent	Injection volume
LPIC separation column made by our laboratory (column dimensions: 10.0×0.5 cm I.D.; particle size: 25–30 μm; exchange capacity: 4.0 mmol g^{-1})	1×10 μs	Ambient	$1.4 \cdot 10^{-3}$ mol l^{-1} Na_2CO_3 aqueous solution	1.2 ml min^{-1}	20 μl

Table 6
Chromatographic conditions for the analysis of light rare earths (La–Eu)

Column	Measurement range	Column temperature	Eluent	Flow rate of eluent	Injection volume
LPIC separation column made by our laboratory (column dimensions: 2.5×0.5 cm I.D.; particle size: 20–25 μm; exchange capacity: 0.02 mmol g^{-1})	2.5×10 μs	Ambient	A mixed aqueous solution of 0.50 mmol l^{-1} ethylene diamine and 1.00 mmol l^{-1} citric acid	1.0 ml min^{-1}	20 μl

Table 7
Chromatographic conditions for the analysis of heavy rare earths (Gd–Lu)

Column	Measurement range	Column temperature	Eluent	Flow rate of eluent	Injection volume
LPIC separation column made by our laboratory (column dimensions: 2.5×0.5 cm I.D.; particle size: 20–25 μm; exchange capacity: 0.01 mmol g^{-1})	6.7×10 μs	Ambient	A mixed aqueous solution of 2.25 mmol l^{-1} ethylene diamine and 0.0132 mol l^{-1} citric acid	1.6 ml min^{-1}	20 μl

Table 8
Chromatographic conditions for the analysis of acidic and neutral amino acids

Column	Measurement range	Column temperature	Eluent	Flow rate of eluent	Injection volume
LPIC separation column C_4 made by our laboratory (column dimensions: 20.0×0.5 cm I.D.; particle size: 25–30 μm; exchange capacity: 0.02 mmol g^{-1})	2.5×10 μs	Ambient	$1.0 \cdot 10^{-3}$ mol l^{-1} HNO_3 aqueous solution	1.2 ml min^{-1}	20 μl

Table 9
Chromatographic conditions for the analysis of basic amino metals

Column	Measurement range	Column temperature	Eluent	Flow rate of eluent	Injection volume
LPIC separation column C_5 made by our laboratory (column dimensions: 4.0×0.6 cm I.D.; particle size: 25–30 μm; exchange capacity: 0.01 mmol g^{-1})	2.0×10 μs	Ambient	$9.0 \cdot 10^{-3}$ mol l^{-1} potassium citrate aqueous solution	1.3 ml min^{-1}	20 μl

5. Results and discussion

5.1. Choice of the exchange capacity of LPIC columns

Exchange capacity is a key factor in the chromatographic analysis. For the analysis of alkali metals and alkaline earth metals, the separation test of various LPIC columns with different exchange capacity (0.05 mmol g^{-1}, 0.01 mmol g^{-1}, 0.02 mmol g^{-1} and 0.03 mmol g^{-1}) were conducted under otherwise identical chromatographic concentration of the eluent, column length and detection conductivity etc. Four typical chromatograms of alkali from the various packing materials are illustrated in Fig. 1. It can be seen that separation takes place by using the LPIC column whose exchange capacity is 0.01 mmol g^{-1}. If the exchange capacity exceeds 0.1 mmol g^{-1}, the sensitivity decreases sharply and the analytical time increases.

The similar tests were also conducted to separate the transition-metals, inorganic anions, organic acids, light rare earths, heavy rare earths and acidic, neutral amino acids as well as the basic amino acids, the exchange capacity was 0.2, 0.02, 4.0, 0.01, 0.02 and 0.02 mmol g^{-1}, respectively, so that the determined substances can be basely separated.

5.2. Choice of the column dimensions

The column dimensions include the column length and the internal diameter of the column, which also determine the separation results of the determined

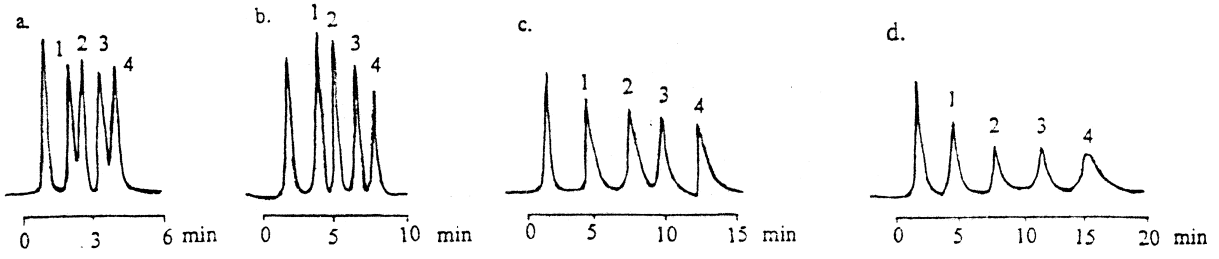

Fig. 1. Separation of alkali metals. Chromatographic conditions are shown in Table 1. Peaks: 1=Li^+; 2=Na^+; 3=NH_4^+; 4=K^+.

substance. Different column dimensions (1.0 cm×0.3 cm I.D., 2.0 cm×0.3 cm I.D., 4.0 cm×0.3 cm I.D., 6.0 cm×0.3 cm I.D., 1.0 cm×0.4 cm I.D., 2.0 cm×0.4 cm I.D., 4.0 cm×0.4 cm I.D., 6.0 cm×0.4 cm I.D., 1.0 cm×0.5 cm I.D., 2.0 cm×0.5 cm I.D., 4.0 cm×0.5 cm I.D., 6.0 cm×0.5 cm I.D., 8.0 cm×0.5 cm I.D., 10.0 cm×0.5 cm I.D., 20.0 cm×0.5 cm I.D., 30.0 cm×0.5 cm I.D., 1.0 cm×0.6 cm I.D., 3.0 cm×0.5 cm I.D., 3.0 cm×0.5 cm I.D., 2.0 cm×0.6 cm I.D., 3.0 cm×0.6 cm I.D., 5.0 cm×0.6 cm I.D., 8.0 cm×0.6 cm I.D., 2.0 cm×0.7 cm I.D., 4.0 cm×0.7 cm I.D., 8.0 cm×0.7 cm I.D.) were tried. For the analysis of various determined substances, the column dimensions vary greatly. The optimum column dimensions are shown in Tables 1–9. Only under these optimum conditions the best separation results can be obtained. Moreover, the pressure differential of LPIC column is very low which is among the range of $1.96 \cdot 10^5$ and $2.94 \cdot 10^5$ Pa. The flow-rate of the eluent can reach 10–20 ml min^{-1}.

5.3. Choice of the particle size of the column fillings

The particle size of the column fillings is also an important factor in determining the separation results. Hence, when the ultra-short columns of LPIC are studied, the particle size of the column fillings must be considered. Different particle size of the column fillings (10 μm, 10–20 μm, 20–25 μm, 25–30 μm, 30–60 μm) were tested. Finally 20–30 μm particle size was chosen. If the particle size was less than 20 μm, the pressure differential of the LPIC column increased, and the retention time of each determined substance became too long. However, if the particle size exceeded 30 μm, the retention time decreased, but the determined substance could not be separated well. Consequently, the optimum particle size of the determined substances are given in Tables 1–9.

5.4. Study of the elution system

The elution system includes the composition and concentration of the eluent, pH and the flow-rate of the mobile phase.

Different eluents, i.e., nitric acid, sulphuric acid, citric acid, tartaric acid, lactic acid, malic acid, oxalic acid, potassium oxalate, sodium carbonate, potassium carbonate, ethylene diamine and their mixed solutions were tried for the various determined substances, respectively. Nitric acid was the best eluent for the analysis of inorganic anions, sodium carbonate was chosen. A mixed solution of citric acid and etylene diamine was excellent for the analysis of the alkaline earth metals and light rare earths. For the analysis of heavy rare earths, a mixed solution of lactic acid and ethylene diamine was the best choice. Potassium citrate was suitable for the analysis of basic amino acids. For the analysis of Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+} and Fe^{2+}, a mixed solution of oxalic acid and citric acid was satisfactory; for the analysis of Zn^{2+}, Pb^{2+}, Fe^{2+}, Cd^{2+} and Mn^{2+}, a mixed solution of tartaric acid and citric acid was excellent.

The concentration of the eluent was close correlative with the pH in the eluent. Therefore, the preparation of the eluent also controlled the pH. The concentration and pH mainly influenced the separation results and the retention time of each determined substance. In this paper, the analysis of basic amino acids were cited as examples. The potassium citrate aqueous solutions with various concentrations ($1.0 \cdot 10^{-3}$, $20 \cdot 10^{-3}$, $40 \cdot 10^{-3}$, $50 \cdot 10^{-3}$, $60 \cdot 10^{-3}$, $80 \cdot 10^{-3}$, $90 \cdot 10^{-3}$, $100 \cdot 10^{-3}$, $120 \cdot 10^{-3}$ mol l^{-1}) were tried for the analysis of basic amino acids (His, Lys and Arg). $90 \cdot 10^{-3}$ mol l^{-1} potassium citrate aqueous solution was the best choice. Different pH values greatly affected the retention time. At pH 3.5, 4.0, 4.5 and 5.0, the retention times (t_R) of His, Lys and Arg varied greatly. At pH 3.5, the retention times were too long, t_R was 10, 15 and 50 min for His, Lys and Arg, respeectively. At pH 4.5 and 5.0, His and Lys could not be separated. Therefore, 4.0 was chosen as the just pH value. At pH 4.0, t_R values were 8, 13 and 26 min for His, Lys and Arg, respectively. The optimum composition and concentration of the eluents for the determined substances are summarized in Tables 1–9.

The flow-rate of the mobile phase also affects the analysis of the determined substances. Different flow-rates were studied, a value of 1.0, 1.0, 1.2, 1.0, 1.2, 1.6, 1.2 and 1.3 ml min^{-1} was appropriate for alkali metals, alkaline earth metals, transition metals,

inorganic anions, organic acids, light rare earths, heavy rare earths, acidic and neutral amino acids and basic amino acids. Under these conditions, the chromatograms show good resolution.

6. Conclusion

The eight typical separation chromatograms of the determined substances are illustrated in Fig. 2, from

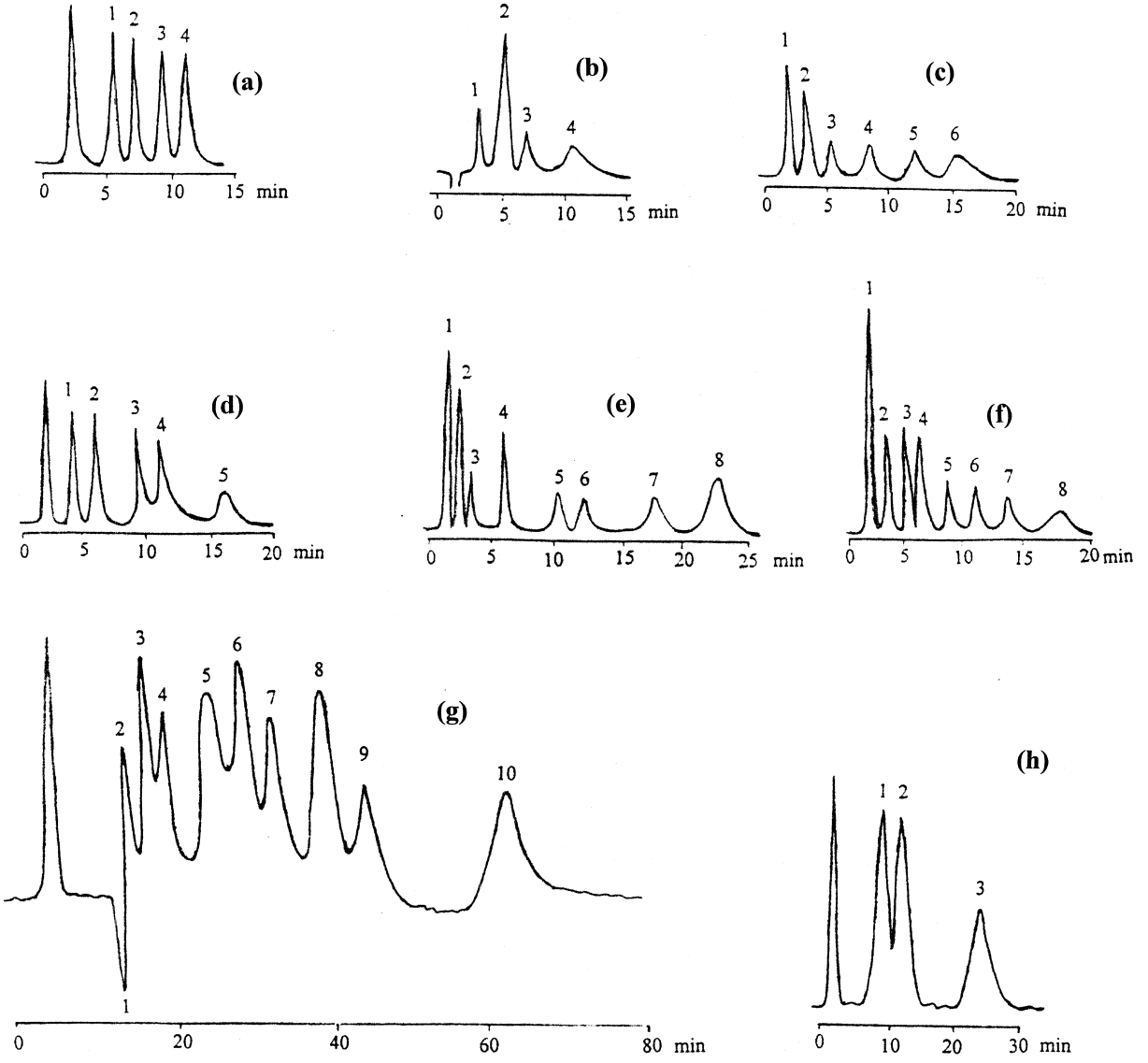

Fig. 2. Typical chromatograms. Chromatographic conditions are shown in Table 1. (a) Alkali metals; peaks: 1=Li^+; 2=Na^+; 3=NH_4^+; 4=K^+. (b) Alkaline earth metals; peaks: 1=Mg^{2+}; 2=Ca^{2+}; 3=Sr^{2+}; 4=Ba^{2+}. (c) Metal cations; peaks: 1=Zn^{2+}; 2=Pb^{2+}; 3=Fe^{2+}; 4=Cd^{2+}; 5=Mn^{2+}. (d) Rare earths; peaks: 1=Eu; 2=Nd; 3=Pr; 4=Ce; 5=La. (e) Inorganic anions; peaks: 1=F^-; 2=Cl^-; 3=Se(IV); 4=$H_2PO_4^-$; 5=Br^-; 6=NO_3^-; 7=SO_4^{2-}; 8=Se(VI). (f) Organic acids; peaks: 1=malic acid; 2=formic acid; 3=succinic acid; 4=acetic acid; 5=propionic acid; 6=butyric acid; 7=valeric acid. (g) Acidic and neutral amino acids; peaks: 1=Asp; 2=hyp; 3=Thr+Ser; 4=Glu; 5=Pro; 6=Ala+Gly; 7=Val; 8=Met; 9=Leu+Ile; 10=Phe. Basic amino acids: peaks: 1=His; 2=Lys; 3=Arg.

the chromatograms, it can be concluded that excellent separation results can be obtained on the ultrashort columns of LPIC.

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